



Long Term Groundwater Monitoring Program – Development of Field Analytical Technologies for the Detection of Military Unique Chemicals

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DoD Environmental Monitoring and Data Quality
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LTM Focus Area

Long Term Monitoring (LTM) of groundwater:

- **Required component of closure on many DoD sites undergoing restoration.**
- **All military services, other Federal agencies (e.g. DoE), states, and responsible parties share similar responsibility.**
- **Costs associated with sampling and laboratory analysis over 10 years estimated to approach \$500M.**
 - **70% of the total monitoring cost.**
 - **50% of the total investigation cost.**
- **Generation of large quantities of waste material**
- **Long time periods from collection to data report**





LTM Focus Area

- **Field analysis of sites for compounds of interest could significantly alleviate some of the issues facing LTM projects.**
 - **Eliminate sample transport**
 - **Replace expensive fixed laboratory analytical costs and reduce analysis time**
- **Available field analytical methods may not be appropriate for military unique compounds (MUCs)**
 - **Quality of data obtained (screening)**
 - **Delicate instrumentation unable to tolerate field conditions**
 - **Instrumentation operational requirements not compatible with field use**
 - **Inadequate instruments and/or technologies for detection of MUCs**





LTM Focus Area

The mission of the LTM Groundwater Program of the Engineering Research and Development Center (ERDC) of the US Army Corps of Engineers is to develop effective field analytical technologies that are acceptable to all levels of the regulatory community and also meet the stewardship and fiscal needs of the Army.

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LTM - Requirements

Technologies that are being developed within the LTM program will address the following according to the A(1.1.a) EQT Operational Requirements Document (EQT-ORD)

- **Applicable to MUCs such as explosive, DU, propellants (e.g. ClO_4^-), pyrotechnics, and degradation products.**
- **Quick analytical turnaround time (<4hrs)**
- **Cost reductions of 25-50% compared to traditional laboratory analysis**
- **Portability, Remote and *In Situ* Operation**
- **Detection of MUCs at levels of concern with defensible data generation**
- **Acceptability to all level of regulatory community (meet requirements of & accepted for SW-846)**





LTM - Thrust Areas

➤ Interim Improvements



➤ Leap Ahead Technologies

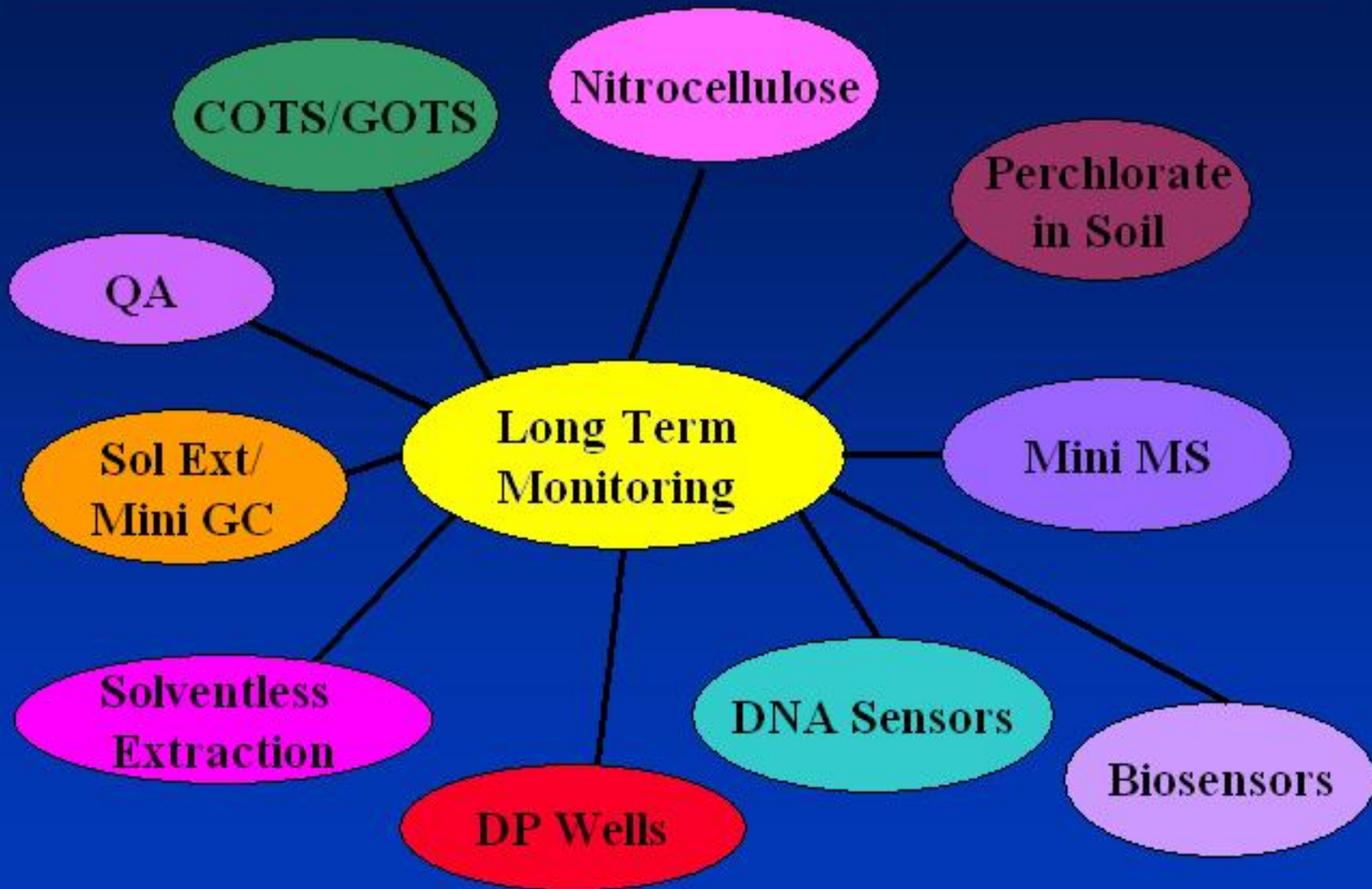


➤ Special Analytical Method Development



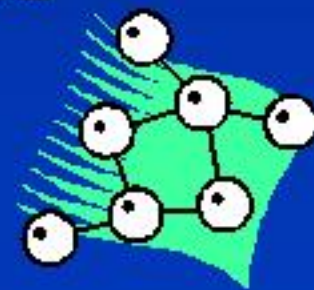


Long Term Monitoring Focus Area



LTM - Interim Improvements

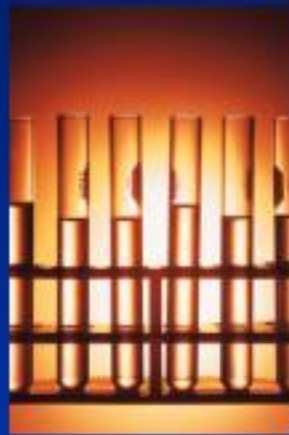
- QA Processes & Protocols
- COTS/GOTS
- Direct Push Wells & Samplers
- Solventless Extraction Technologies
- Solventless Extraction Technologies Interfaced to Miniature GC



LTM - Interim Improvements

QA Processes & Protocols

POC: Rich Meyer – Environmental Laboratory, ERDC



- **Identify Essential QA/QC for Field Analytics**
- **Identify Reduced Cost Steps for Fixed Lab**
- **Evaluate Proposed Processes & Protocols**
- **2004 ERDC Technical Report**

**Key Component of LTM Technologies
is Ability to Generate Definitive Data**

LTM - Interim Improvements

COTS/GOTS

POC: Dave Splichal – Environmental Laboratory, ERDC

- **2004 ERDC Technical Report**

- **Sampling Devices**

- **Field Instrumentation – GC/MS**

- **Sensors**

- **Applicability to LTM**

- **Detection Limits**

- **Quality Control**

- **Cost Savings**



LTM - Interim Improvements

Solventless Extraction Technologies

**POC: Dave Splichal & Denise MacMillan
- Environmental Laboratory, ERDC**



- **Identify & Develop Solventless Extraction Technologies**
- **Perform Lab & Field Studies**
- **Investigating use of Twister and SPME for MUCs**
- **Evaluation of Potential for On-Site Extraction**



LTM - Solventless Extraction

Preliminary Results for On-Site Extraction of Explosives

<u>Analyte</u>	<u>% Recovery</u>	<u>Method 8330 Control Chart, % Recovery</u>
HMX	100	39-126
RDX	72	35-119
Tetryl	131	14-120
TNT	92	71-117
2,4-DNT	99	76-110

LTM - Interim Improvements

Solventless Extraction Technologies Interfaced to Miniature GC

**POC: June Mirecki & Dave Splichal –
Environmental Laboratory, ERDC**

- **Develop Field Analytical Capability for Twister & SPME**
- **Perform Lab & Field Studies for Explosives Detection**
 - **Characteristic Spectra (GC/MS)**
 - **Sensitive and Precise**
 - **Quality Control**





LTM - Interim Improvements

Direct Push Wells & Samplers

**POC: Louise Parker – Cold Regions
Research Laboratory, ERDC**



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LTM - Direct Push Wells

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**Conventional
(Hollow-Stem Auger)**

PVC well casing

Slotted screen

**Bentonite
or cement
grout**

**Bentonite
seal**

Sand filter

**Direct Push
(Pre-packed Screen)**

PVC casing

**Natural
aquifer
material**

**Sand filter
inside
S.S. mesh**

**Expendable
drive
point**

**Direct Push
(Exposed Screen or
Well Point)**

**No
Seal**

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Promising Discrete-Interval Devices

Diffusion Sampler – Membrane Varies

- Goal is to find a membrane/device that works for explosives
- Initial studies have focused on a jar-type sampler with open end covered with Nylon membrane
- Developed by Don Vroblesky (USGS)





Jar-Type Sampler Study

US Army Engineer Research & Development Center

Day 7	<u>Control</u>	<u>Sampler</u>	<u>Difference</u>
HMX	1.63	1.55	-4.8
TNB	14.6	14.2	-2.7
RDX	9.20	8.90	-3.3
1,3-DNB	0.635	0.619	-2.4
TNT	2.66	2.58	-3.2
2,4-DNT	0.095	0.092	-2.8
Day 35			
HMX	1.46	1.46	0
TNB	13.3	13.1	-1.5
RDX	8.18	8.22	+0.5
1,3-DNB	0.564	0.564	0.0
TNT	2.32	2.32	0.1
2,4-DNT	0.080	0.078	-2.6





Re-designed Hydrasleeve

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VOC Testing

and



**Turbidity
Evaluations**





Snap Sampler

- Spring activated
- No sample transfer
- VOCs, explosives & pesticides



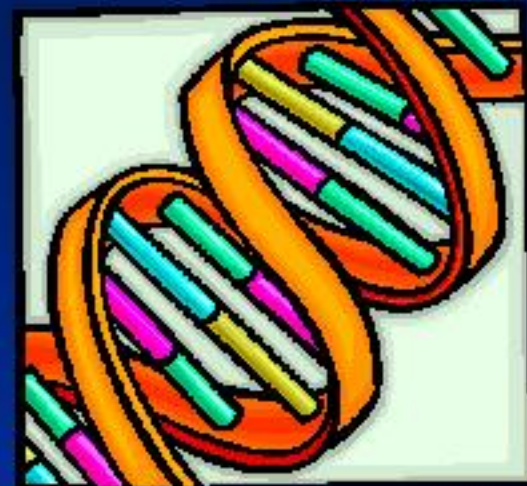


LTM - Leap Ahead Technologies

Catalytic DNA Sensors

POC: Don Cropek – Construction Engineering Research Laboratory, ERDC

Collaboration with Dr. Yi Lu, University of Illinois



- **Specific - Reacts with a single chemical, reliable without false positives**
- **Sensitive - Ultra-low concentration**
- **Flexible - Detector for many different compounds**
- **Convenient - Fast, small sensor array**



LTM - Catalytic DNA Sensors

US Army Engineer Research & Development Center

**Contaminated Water or
Vapor Signature**



**Explosive-
sensitive DNA**



**DNA reacts
with vapor
signature**

**Reaction
cleaves the
DNA, causing
detectable
fluorescence.**

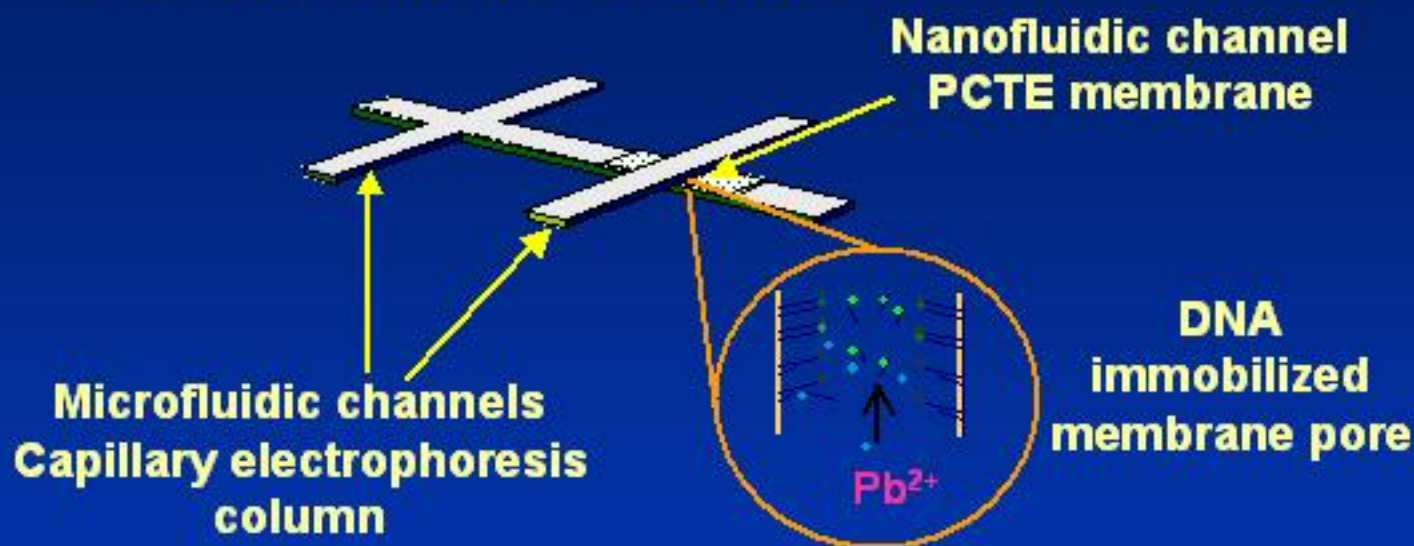


Sensor array



LTM - Catalytic DNA Sensors

Nanofluidic Molecular Gate Membranes



Expanded view of the microfluidic channels and the nanofluidic molecular gate membrane.



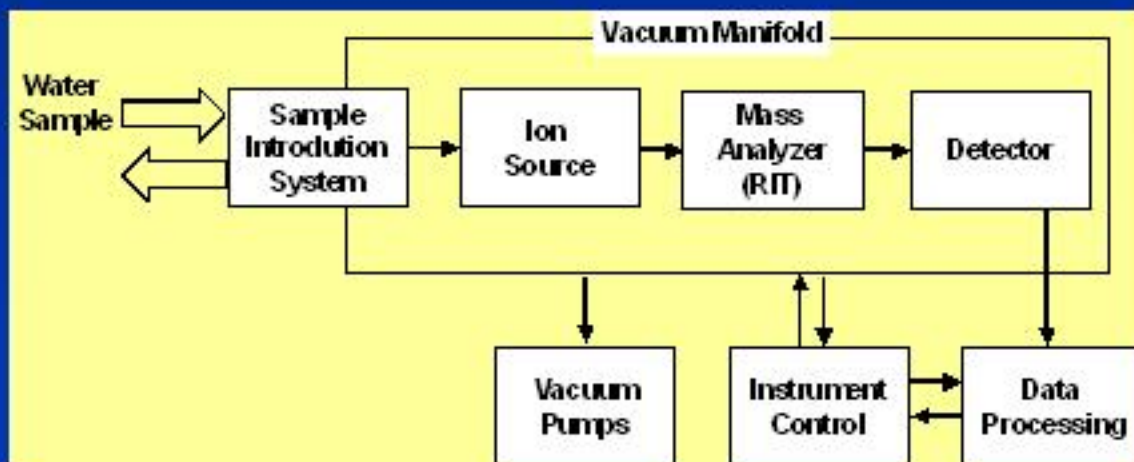
LTM - Leap Ahead Technologies



Miniature Mass Spectrometer

**POC: Denise MacMillan –
Environmental Laboratory, ERDC**

**Collaboration with Dr. Graham Cooks,
Purdue University**

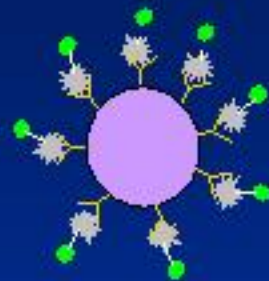




LTM - Leap Ahead Technologies

Microfluidic Biosensors

POC: Shana Dalton – Environmental Laboratory, ERDC

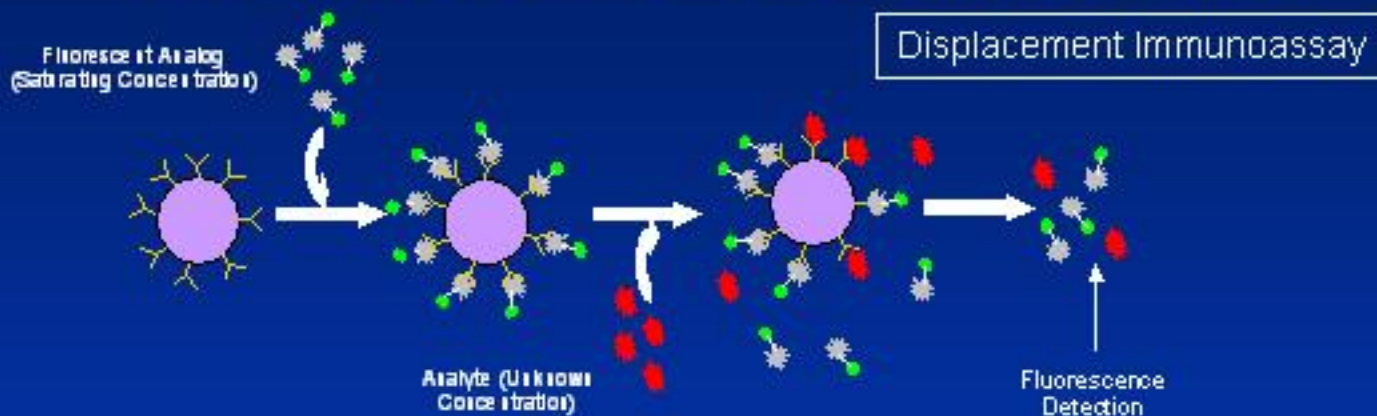


- **Develop Sensitive & Selective *In Situ* Detection Capability for Military Unique Compounds with Antibody Capture Technology (Immunoassay)**
 - **Rapid (minutes), Sensitive (ppb or ppt), Specific, Small**
- **Fluorescent-linked detection**



LTM - Microfluidic Biosensors

- Immunoassays with commercially available RDX and TNT antibodies immobilized on magnetic beads



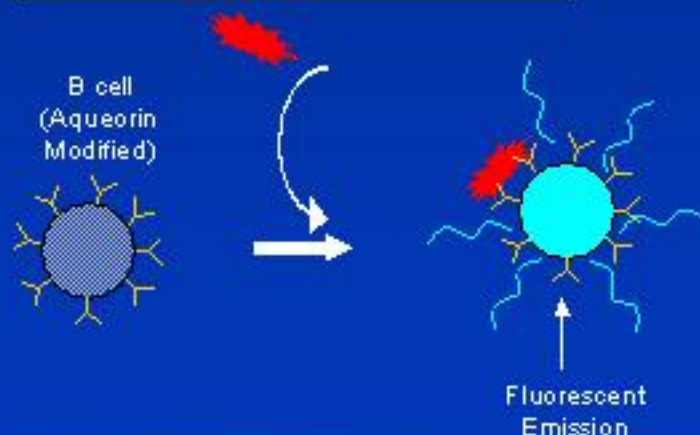
- Expand the number of antibodies to MUCs
 - Developing antibodies to HMX and 2, 4-DNT with Strategic Biosolutions (~ 9 months / analyte)
- Collaborate with other laboratories currently developing immunoassay-based technologies

LTM - Microfluidic Biosensors

CANARY (Cellular Analysis and Notification of Antigen Risk and Yields)

- Developed at MIT-LL
- Excellent for Biological Agents
 - *Bacillus anthracis* (anthrax)
 - *Yersinia pestis* (plague)
 - FMD (Foot and Mouth Disease) virus
 - *E. coli*
- Highly sensitive response in seconds
- Detection of Toxins (Small Molecules)
 - Developmental Stage

CANARY Bioassay



Lightweight COTS Components



Battery-powered operation > 6 hours
Luminometer dimensions: 7" x 4" x 5 1/2"
Total weight < 4 pounds including batteries

Source: Presentation at Federal Bio-
Chem Detection Conference, Oct. 2003
by Peter Emanuel, PhD, Critical
Reagents Program Director, JPE-CBD



LTM - Special Analytical Methods



Nitrocellulose:

- **Gun cotton, pyroxilin, ~12% N**
- **Occurs with nitroglycerin at firing points**
- **Differential solubility method under development**

Perchlorate:

- **Used primarily as a solid rocket fuel**
- **Other sources include flares, airbags, fireworks, some nitrate-based fertilizers**
- **Competes with iodine in thyroid - low action level expected**
- **Through soils with little, if any, adsorption occurring**
- **Experiments designed & conducted to test ClO_4^- adsorption to soil under both oxic & anoxic conditions**





Focus Area Project Delivery Team

- **Project Delivery Team: ERDC, AEC, and CEHNC**
 - Co-chaired by ERDC and AEC.
 - General oversight & dispute resolution by Environmental Technology Integrated Process Team (ETIPT).
- **ERDC - S&T (BA1-BA3)**
 - Dr. M. John Cullinane – Manager for S&T effort.
 - Dr. Denise MacMillan - S&T Focus Area Manager.
- **AEC - T&E (BA4-BA6)**
 - Mr. James Daniels Manager for T&E effort.
 - Mr. William Houser - T&E Focus Area Manager.
- **DOD Coordination Group**
 - Effort Managers.
 - Focus Area Managers.
 - Rep from CEHNC, JUXOCO, SERDP/ESTCP.
 - Rep from other service.



LTM Focus Area

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